EFFECT OF HIGH TEMPERATURE SHORT TIME HEAT TREATMENTS ON SOME PHYSICAL AND CHEMICAL PROPERTIES OF MILK

BY

JOHN HENRY HETRICK

B. S., Pennsylvania State College, 1938

M. S., Ohio State University, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN DAIRY HUSBANDRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1947

URBANA, ILLINOIS

1947

EFFECT OF HIGH TEMPERATURE SHORT TIME HEAT TREATMENTS ON SOME PHYSICAL AND CHEMICAL PROPERTIES OF MILK

BY

JOHN HENRY HETRICK

B. S., Pennsylvania State College, 1938

M. S., Ohio State University, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN DAIRY HUSBANDRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1947

URBANA, ILLINOIS

1947

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. P. H. Tracy for his help and guidance not only in the direction of the thesis work but throughout all the graduate work pertaining to the fulfillment of the requirements of this degree.

The author also wishes to thank the Executive Faculty of the University of Illinois for permitting this work to be done in absentia. He further wishes to express his appreciation to Mr. Sam Dean, Jr., President, and Dr. W. J. Corbett, Technical Director, of the Dean Milk Company for permission to use the facilities of the company research laboratory and for their encouragement and generous allotment of time for this work.

The cooperation of Illinois Creamery Supply Company, Chicago, Illinois, in supplying the small tube heat exchanger (the Mallory unit) used in this work is gratefully acknowledged.

To his associates, Dr. R. M. Whitney, Mr. A. R. Kemp, Mr. W. J. Mautino, Mr. E. L. Kaney, and Mr. K. L. Keane, the author extends his sincere thanks for their active assistance in certain phases of the work.

R. UNIV. BIBLIOTHEEK LEIDEN

EFFECT OF HIGH TEMPERATURE SHORT TIME HEAT TREATMENTS ON SOME PHYSICAL AND CHEMICAL PROPERTIES OF MILK

The heating of milk for human consumption has been practiced for many years. It was not, however, until after Louis Pasteur's discovery (1860) that controlled heat treatments were used for the purpose of destroying harmful micro-organisms. In recent years the heating of milk sold for public consumption has been widely practiced. The chief aim in heating the milk has been to make the product safe. Milk is heated, too, to improve its keeping quality and in a product such as evaporated milk, the aim is to heat treat with sufficient intensity that all micro-organisms are destroyed. The preheating process followed in the manufacture of evaporated milk serves also to regulate the heat stability of the milk proteins. Heating also improves the digestibility of the milk for infant feeding, improves the keeping quality of certain manufactured products, and renders milk more acceptable for use in other food products such as confections and bread.

Some of the more common changes which are known to occur if milk is heated at or slightly above pasteurizing conditions are: reduction in the activity of the enzymes, development of a cooked flavor, reduction in creaming ability, increase in the rennet coagulation time, a reduction in number of bacteria, and a reduction in the vitamin B_1 and vitamin C contents.

By the use of longer holding periods or by use of temperatures higher than those commonly used for pasteurization, changes occur in the redox potential due to the formation of reducing substances, some denaturation of albumen and globulin occurs, the curd tension becomes lower,

the flavor becomes more "cooked," and more bacteria are killed. Changes also occur in the salt equilibria and in the water binding capacity of the colloids and the rennet coagulation time is extended.

Under extreme conditions of heat treatment (sterilizing and above), all the bacteria are killed, the albumen and globulin become completely denatured, the lactose caramelizes, the casein hydrolyzes, aldehyde-amine complexes are formed, the milk becomes brown, lactic and formic acids are formed, and the flavor becomes objectionable.

The ideal goal would be to heat milk to produce the desirable effects without causing any undesirable changes which would be reflected in the flavor, nutritional value, and general appeal of the product. The results of the work of previous investigators on the quantitative effects of time and temperature of heating on the properties of milk have indicated that some progress can be made toward attainment of this goal by higher temperature and shorter time processing. Most of these investigators have been handicapped in their studies, however, because, with the equipment they used, comparatively long periods of time were required to heat the milk to the desired temperatures. Possibly because of lack of proper heating equipment, there has been little or no work reported on the effects of short time heating of milk on its physical and chemical properties at temperatures higher than the boiling point.

In 1942, Mallory (1) patented a process for heat treating which is adaptable to the continuous sterilization of milk. By application of the principles of fluid flow, he designed a small tube heater through which the milk would flow at such a high velocity and degree of turbulence during heating and cooling that no laminar film would form. Consequently, heat exchange was much faster and, according to the information in the patent (1), the unit was capable of heating milk to 300°F. in 5 seconds. Under these conditions the milk could be sterilized without a change in flavor (1).

In June, 1946, an experimental unit built on Mallory principles by Illinois Creamery Supply Company, Chicago, Illinois, was installed in the research laboratory of the Dean Milk Company, Rockford, Illinois.

In view of the facilities at hand, it seemed desirable to reinvestigate the effects of heat treatment on certain properties of milk where extremely short heating and cooling times are used, and to extend the study to investigate the effects produced at temperatures higher than have previously been studied. The effects of heat on the following properties were considered in this investigation: phosphatase activity, lipase activity, creaming ability, bacteria count, rennet coagulation time, flavor, curd tension, and denaturation of albumen and globulin.

Experimental Methods

All the experimental work was done in the research laboratory of the Dean Milk Company in Rockford, Illinois. The milk used for the study was fresh, grade A, raw milk as received at the plant from the Company's patrons. The Mallory small tube heat exchanger was used to process the milk. This unit had a capacity of 80 gallons per hour. It was composed of five independently operating heating sections and two cooling sections. Milk was forced through the unit with an 80 gallon per hour Manton-Gaulin homogenizer used as a high pressure pump. A pressure of 800-1000 lbs./in.^{2} was required to force the milk through the unit. Each heating section was composed of four 58½″ lengths of ¼″ o.d. stainless steel tubing through which the milk flowed, surrounded by a larger pipe containing dry steam as the heating medium. The cooling sections were similarly constructed except that refrigerated water was pumped through the outer tubes for cooling purposes. The time required for the milk to flow through one heating or cooling section was calculated to be 0.83 sec. and the milk flowed through the unit at a calculated velocity of 23.6 feet per second. Temp-

eratures were regulated by an air-actuated steam pressure controller and measured with an iron-constantan thermocouple which was soldered to the tube wall at the outlet of the heating section. Holding for various times was accomplished in two different ways. For temperatures below boiling, a copper coil $\frac{3}{8}$ in o.d. immersed in a water bath held at the desired holding temperature was connected to the outlet of the heating section. For holding at temperatures above boiling, holding tubes of various sizes which would yield holding times of 13 sec., 26 sec., and 64 sec. were connected from the outlet of the heating section to the inlet of the cooling section. In cases where milk was held, the temperatures were measured with a mercury-in-glass thermometer, inserted in a mercury well, which was placed in the line just ahead of the cooling section.

In the studies involving time temperature relationships for the inactivation of phosphatase and lipase, destruction of the cream line and increase in the rennet coagulation time, the time required to heat to all temperatures was calculated to be 0.83 seconds and, after holding at these temperatures for the desired time, the phosphatase and lipase samples were immediately cooled in ice water. The milk for the cream line and rennet coagulation time observations was processed in a continuous manner by heating, holding, and cooling in the Mallory unit. A calculated time of 1.66 seconds was required to cool to below 100°F. The samples were immediately cooled further in ice water. In the studies involving changes in the flavor, curd tension, and the denaturation of albumen and globulin, the calculated time required to heat to all temperatures was 4.2 seconds. After holding, the milk was cooled in the Mallory unit to below 100-130°F. in a calculated time of 1.66 seconds. The samples were immediately cooled further in ice water.

The phosphatase activity was measured by the method of Sanders and Sager (2), using a Coleman model 11 spectrophotometer for measuring the intensity of the indophenol

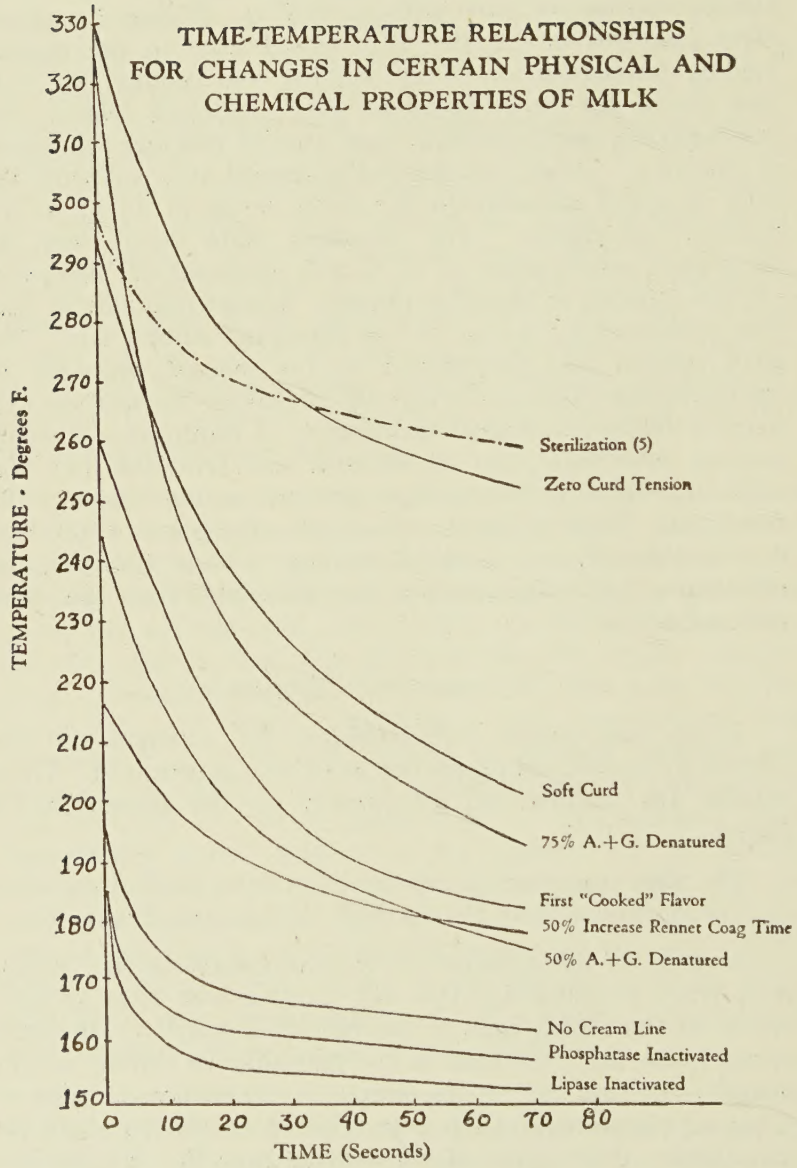
color in the butyl alcohol extract. Lipolysis was induced by homogenization of raw milk (105°F.). Within 5 seconds after homogenization, the milk was heated to the desired holding temperatures. After holding and cooling, the milk was stored for 44-48 hours at 40°F. Surface tension and organeolyptic measurements were used to measure the extent of lipolysis. Cream volume was measured after allowing the milk to stand undisturbed for 20-24 hours at 40°F. in 100 milliliter graduates. The standard plate count with an incubation temperature of 37°C. was employed for determining the number of bacteria present. Rennet coagulation time was measured by means of the Marschall rennet test. The curd tension was determined by the method proposed by the committee of the American Dairy Science Association (3), using a Submarine Signal curdometer. A semi-micro Kjeldahl method essentially that of Menefee and Overman (4) was used to determine the nitrogen content of the various milk fractions. Total nitrogen, non-casein nitrogen and non-heat denaturable nitrogen were determined. Casein nitrogen, and albumen and globulin nitrogen were calculated from the above determinations.

Experimental Results

Time - temperature relationships for changes in the previously mentioned properties have been determined. These results are summarized graphically in the accompanying figure.

The time-temperature relationships for sterilization given in this figure are from the work of Curran and Evans (5).

A study of the distribution of phosphatase in the various milk fractions indicated that the enzyme was more concentrated in the cream than in the skimmilk portion. In order to minimize the difference in the phosphatase activity of the heated milk and the cream separated therefrom, a value of 1 p.p.m. phenol equivalent was selected as the standard for satisfactory destruction of the enzyme in milk. By Sanders


TIME-TEMPERATURE RELATIONSHIPS
FOR CHANGES IN CERTAIN PHYSICAL AND
CHEMICAL PROPERTIES OF MILK
TEMPERATURE - Degrees F.
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
0
10
20
30
40
50
60
70
80
TIME (Seconds)
Sterilization (5)
Zero Curd Tension
Soft Curd
75% A.+G. Denatured
First "Cooked" Flavor
50% Increase Rennet Coag Time
50% A.+G. Denatured
No Cream Line
Phosphatase Inactivated
Lipase Inactivated

and Sager's (2) method of expression, this would be 1 unit per milliliter of milk. The results secured on lipase inactivation by heat indicated that this value was not too severe as a standard for pasteurization because a temperature of 185°F. with a 0.03 sec holding period was required to inactivate the lipase as well as the phosphatase.

Using this value (1 p.p.m.) as the standard, a semilogarithmic relationship between time and temperature over the temperature range of 145-185°F. was found to exist for the thermal destruction of phosphatase. This relationship can be expressed by the following formula:

$$T = 174 - 9 \log t$$

In this formula T is the temperature (°F.) and t is the time (sec.) required at temperature T to inactivate the phosphatase. From this formula, another expression was developed which indicates the destructive effect of each second hold at any temperature T in reducing the phosphatase activity to 1 p.p.m. phenol equivalent. This formula is:

$$D = \text{antilog}_{10} \frac{T - 174}{9}$$

The summation of the D values multiplied by the time in seconds at the corresponding temperatures must be 1 or greater for any time-temperature cycle to satisfactorily inactivate the phosphatase. Data secured with various rates of heating indicate that this mathematical solution is satisfactory for practical use in determining time-temperature relationships necessary to give a negative phosphatase test in milk with various heating methods. It follows that, if the phosphatase test is used as the standard for adequate pasteurization, this mathematical method could be applied to determine proper time-temperature conditions.

Heat treatment of milk with time-temperature conditions sufficient to inactivate the phosphatase also inactivated the

lipase, caused a slight increase in rennet coagulation time, a 97-99.8% reduction in bacteria count, and resulted in a slight decrease in 24 hour cream volume. This decrease in cream volume was attributed to closer packing of the fat globules in the cream layer rather than to less cream rising.

More severe heat treatment was required to produce the first definite cooked flavor than was required to inactivate the phosphatase. The curve in the accompanying figure representing the time-temperature conditions of heating under which the flavor first became definitely cooked coincides with conditions required for the denaturation of 58% of the albumen and globulin and a reduction of about 20% in curd tension.

Under the conditions of these experiments it was not possible by means of heat treatment to reduce the curd tension to such an extent that the treated milk could be called soft curd without causing a cooked flavor. To be called soft curd milk must have a curd tension of 20 grams or less (3). Milk which was sufficiently heat treated to attain sterility always possessed a definitely cooked flavor. However, with the high temperature short time heating methods employed, much less cooked flavor was present than is commonly found in milk sterilized by the conventional 240°F. long time process. The results of this study, therefore, do not preclude the possibility of sterilizing milk without the production of a cooked flavor by employing even higher temperatures and shorter heating times than were used in this study.

The rate of heating to the desired temperatures was found to be an important factor affecting the changes produced. This was true for changes produced by heat on all the properties studied and the importance of the heating rate became more marked as the temperature to which the milk was heated was increased. It is evident in a study of this nature that it is extremely important to specify not only the temperature to which the milk was heated and the holding

time, but also the time required to heat to and cool from the desired temperature. When the accumulative effects of heat treatment in reaching the desired temperatures were considered, it was possible to correlate the results secured from various heating methods in which the time required to heat differed markedly. It is possible that some of the discrepancies which exist in the literature could be similarly explained if this information was given.

LITERATURE CITED

1. Mallory, Wilhelm E. "Process for treating liquids." U. S. Pat. No. 2,270,540. January, 1942.

2. Sanders, George P., and Sager, Oscar S. "Modification of the phosphatase test as applied to cheddar cheese and application of the test to fluid milk." Jour. Dairy Sci. **29,** 737, 1946.

3. A. D. S. A. "Final report of committee on methods of determining the curd tension of milk." Jour. Dairy Sci. **24,** 825, 1941.

4. Menefee, S. G., and Overman, O. R. "A semi-micro Kjeldahl method for the determination of total nitrogen in milk." Jour. Dairy Sci. **23,** 1177, 1940.

5. Curran, H. R., and Evans, F. R. "Time-temperature relationships for high temperature short time sterilization of evaporated milk." Jour. Dairy Sci. **27,** 909, 1944.

VITA

John Henry Hetrick was born in Beavetrown, Pennsylvania, on September 16, 1916. He entered the Beaver Township elementary school in 1922 and in 1924 he moved to Bedford, Pennsylvania, where he completed his elementary education in 1930. From 1930-1934 he attended Bedford High School, graduating as class salutatorian. In 1934 he entered Pennsylvania State College, majoring in Dairy Manufacturing and minoring in Bacteriology and Agricultural Biochemistry, and in 1938 received a Bachelor of Science degree, graduating with honors. While he was at Pennsylvania State College, he was recipient of the Alpha Zeta Schloraship Award and elected to Phi Eta Sigma, Gamma Sigma Delta, and Phi Kappa Phi. In the summer of 1936 he was employed by Breyer Ice Cream Company, New York, N. Y., and the summers of 1937 and 1938 were spent in the employ of the Supplee Wills Jones Milk Company in the laboratory of their condensed milk manufacturing plant in Chambersburg, Pennsylvania.

In 1938-1939 he served as graduate assistant in the Dairy Technology Department at Ohio State University, during which time he completed the requirements for the degree of Master of Science. For the next year and a half he was employed by Supplee Wills Jones Milk Company, Philadelphia, Pennsylvania, working first in the laboratory and then as plant manager of their Chambersburg plant. In August, 1941, he accepted a position with Price's Creamery, Portales, New Mexico, where he worked on milk procurement and in charge of milk processing. From December, 1941, to June, 1943, he was instructor in Dairying at Oklahoma A. and M. College, Stillwater, Oklahoma. In June, 1943, he accepted a position as Associate in Dairy Manufactures at the University of Illinois, Urbana, Illinois. While here he continued his graduate work and in June, 1945, he resigned his position at the University and accepted a position

in the research laboratory of the Dean Milk Company, Rockford, Illinois. In 1946, he was made Research Supervisor, which is his present position.

He was elected to Sigma Xi in 1946. He is a member of the American Dairy Science Association and the Institute of Food Technologists.

He has presented a total of ten papers at technical meetings, dealing with his work on the oxygen content, the solubility, and the keeping quality of whole milk powder, the keeping quality of frozen milk, frozen condensed milk, and frozen cream, the determination of copper in milk powder, the use of sodium alginate in ice cream, and homogenization efficiency studies. His publications are:

Hetrick, J. H., and Tracy, P. H. "Determination of copper in milk powder by a direct carbamate method." Jour. Milk Tech. **8**, 1, 1945.

Hetrick, J. H., and Tracy, P. H. "Some observations on the keeping quality of spray-dried whole milk stored at room temperature." Jour. Dairy Sci. **28**, 687, 1945.